2.0 THEORY OF LFG EMISSIONS

LFG emissions are primarily governed by the following variables:

- gas-generation mechanisms,
- factors influencing gas generation,
- gas-transport mechanisms, and
- factors influencing gas transport.

The following sections discuss these issues.

2.1 GAS-GENERATION MECHANISMS

LFG is produced from one or more of three mechanisms:

- evaporization/volatilization,
- biological decomposition, and
- chemical reactions.

Physical, chemical, and biological processes transform solid waste after it is deposited in a landfill. The waste is first compressed by landfill equipment, and subsequently compacted by more waste and daily cover materials. In addition to the initial compression and compaction, the landfill undergoes settlement for many years. This settlement occurs as the waste further consolidates and biological decomposition reduces the waste volume. The landfill's final waste thickness may be reduced by as much as 30 percent due to settlement.

Water infiltration through the cover material, percolation of water contained within the original waste, and water produced as a product of waste decomposition, all form a medium in which soluble substances dissolve and generate leachate. Chemical and biochemical reactions within the landfill mainly involve the products of the decomposing waste, hydrogen, organic acids, CH_4, and CO_2.

2.1.1 Evaporation/Volatilization

Vaporization action is due to the change of chemical phase equilibrium that exists within the landfill. Some gas-generating materials will be present in the waste mass as it is received and deposited in the landfill. Organic compounds in the landfill cells will vaporize until the equilibrium vapor concentration is reached. This process is accelerated when the waste becomes biologically active, as a result of heat, which is evolved within the landfill as part of the biological process. The rate at which components are evolved depends on physical and chemical properties of the compounds. The most significant of these parameters are the Henry's Law Constant, which describes the equilibrium partitioning between the vapor and aqueous phases at a given pressure and temperature.

Henry's Law Constant. Henry's Law determines the extent of volatilization of a contaminant dissolved in water.

Henry's Law states: The weight of any gas that will dissolve in a given volume of liquid, at constant temperature, is directly proportional to the pressure that the gas exerts above the liquid.

Henry's Law is presented in the following formula:

$$P_A = H_A * X_A \tag{2-1}$$

where,

P_A = partial pressure of compound A in the gas phase.

X_A = mole fraction of compound A in liquid phase in equilibrium with the gas phase

H_A = Henry's constant.

Henry's constant quantifies the tendency for a liquid compound in solution (i.e., in groundwater or soil moisture) to partition to the vapor phase. This constant is temperature-dependent, increasing with an increase in temperature. In general, liquid compounds with Henry's constants greater than 10^{-3} atm.m^3/mol are considered to have high vapor-phase partitions. When using Henry's constant for various compounds, care must be taken to use a consistent system of units. The table below summarizes the various forms of Henry's constant and appropriate units:

Units and Conversion Factors for Henry's Constant

P Concentration in Gas Phase	X Concentration in Liquid Phase	Henry's Constant	
		Symbol	Units
atm	mol fraction	H_C	atm
atm	mol/m^3	H	atm-m^3/gmol
g/m^3	g/m^3	$H_{A'}$	dimensionless
mol fraction	mol fraction	$H_{A'}$	dimensionless

Conversion factors for Henry's Constants

1. $H = (VP * MW)/S$
where,

H = Henry's Constant, atm-m^3/gmol
VP = vapor pressure of pure substance, atm
MW = Molecular weight, g/gmol
S = Solubility of gas, g/m_3

2. $H_C = H * C_0$
where,

H_C = Henry's Constant, atm
C_0 = Molar Density of Water, 55.6×10^3 gmol/m^3
  or   55.6 kmol/m_3
  or   55.6 gmol/L

3. $H_{A'} = H_C/(C_0 * R * T)$
where,

$H_{A'}$ = Henry's Constant, dimensionless
R = Universal Gas Constant, 8.2×10^{-5} atm-m^3/gmol-T
T = degrees Kelvin

Estimated Henry*s constants for some organics at 20°C (68°F) are shown in Table A-1.

2.1.2 Biological Decomposition

Sanitary landfills produce large quantities of gas, with the major component being CH_4. LFG generation occurs as a result of two conditions, aerobic and anaerobic decomposition. Generally, aerobic conditions degrade the larger molecules into

TABLE A-1

Henry's Constant of Common Organic Compounds

Compounds	H atm.m^3/gmol	H$_c$ atm	H$_A'$ Dimensionless
Vinyl chloride	6.4	3.56 x 10^5	266
Dichlorofluoromethane	2.1	1.17 x 10^5	87.6
Methane	0.63	3.50 x 10^4	26.2
1,1-Dichloroethylene	1.7 x 10^{-1}	9.45 x 10^3	7.07
1,2-Dichloroethylene	1.7 x 10^{-1}	9.45 x 10^3	7.07
Chloroethane	1.5 x 10^{-2}	8.34 x 10^2	0.62
Trichloroethylene	1.0 x 10^{-2}	5.56 x 10^2	0.42
1,1,1-Trichloroethane	3.6 x 10^{-3}	2.00 x 10^2	0.15
Chloroform	3.4 x 10^{-3}	1.89 x 10^2	0.14
Methylene chloride	2.5 x 10^{-3}	1.39 x 10^2	0.10
1,1,2-Trichloroethane	7.8 x 10^{-4}	4.34. x 10^1	0.032
Naphthalene	3.6 x 10^{-4}	2.00 x 10^1	0.014
Phenol	2.7 x 10^{-4}	1.50 x 10^1	0.0011
Source: Adapted from Reference 4			

smaller and smaller molecules leading to anaerobic degradation of
organic acids which generates CH_4 and CO_2. It is important to
understand
that there will be mixed aerobic and anaerobic degradation
occurring at the same time. The facultative, degrading microbes
(capable of growing and surviving with or without O_2) perform the
necessary dual functions of degrading larger molecules and
consuming O_2 to create and sustain the anaerobic environment
which favors CH_4 production.

These processes normally occur in three stages: aerobic,
anaerobic/thermophilic, and anaerobic/methanogenic. The bacteria
involved in biological decomposition exist in the refuse and soil
used in landfill operations. Seeding the refuse with bacteria
from another source can result in a faster rate of development of
the bacterial population.

The gas release rate into the waste void space is
principally affected by the pH and the rate of water production
in each of the modes of bioprocessing. Since water is a normal
product of the first stage (aerobic), more water may be present
in the matrix than would normally be expected based on the water
content of the wastes. This water will compete for space with
the air during compaction and will dissolve some of the
bioreaction gases. The first two stages reduce the pH of the
water and may affect the evaporation/volatilization rate
accordingly.

2.1.3 Aerobic Decomposition

Aerobic decomposition begins shortly after the waste is
placed in the landfill and continues until all of the entrained
O_2 is depleted from the voids and from within the organic waste.
Decomposition products under aerobic conditions are CO_2
(primarily), water, and nitrate. Aerobic bacteria produce a gas
characterized by high temperatures (54 to 71°C or 130 to 160^{0}F),
high CO_2 content (30 percent), and low CH_4 content (2 to 5
percent).

Aerobic decomposition may last for as little as 6 months to
as long as 18 months for waste in the bottom lifts of the
landfill. However, in the upper lifts of the landfill, aerobic

decomposition may last for as little as 3 to 6 months if CH_4-rich gas from lower lifts flushes O_2 from the voids in the upper lifts. Aerobic decomposition produces the conditions and byproducts necessary for anaerobic decomposition. Limited aerobic decomposition from infiltration of O_2, as air or dissolved in water, into the landfill may continue for years. This continuing okidative degradation by aerobic and facultative organisms can continue to drive the subsequent anaerobic processes. Aerobic degradation generally degrades many of the larger polymers in the wastes, such as starches, cellulose, lignins, proteins, and fats into smaller, more available oligomers (polymer consisting of 2 to 4 monomers) which can then be further degraded into dimers (molecule consisting of two identical simpler molecules) and monomers such as sugars, peptides, amino acids, long-chain fatty acids, glycerol and eventually organic acids, as discussed below. These less complex products of aerobic degradation are more readily degraded anaerobically than the larger polymers.

2.1.3.1 <u>Anaerobic Decomposition</u>
     Anaerobic decomposition occurs in two distinct processes. When all of the entrained O~ is depleted from the waste, the waste decomposition changes from aerobic to anaerobic, and two new groups of bacteria emerge which thrive in anaerobic (no O_2) environments. Facultative microbes convert the simple monomers into mixed acid products along with hydrogen and CO_2. Anaerobic bacteria convert the mixed volatile organic acids (e.g., formic, acetic, propionic and butyric acids), aldehydes and ketones into primarily acetic acid and hydrogen, using water in place of O_2. These organic acids reduce the pH, which increases the solubilization of some organic and inorganic wastes, thereby increasing the concentration of dissolved solids in the leachate. CH_4 production can be limited during this stage since the low pH (5 to 6) is somewhat toxic to the methanogenic (methane-producing) bacteria. During the second anaerobic process, the methanogenic bacteria become more prominent. These methanogens degrade the volatile acids, primarily acetic acid and use the hydrogen to generate CH_4 and CO_2 (typically in a 1:1 ratio). This degradation results in a more neutral pH (7 to 8), a decrease in the COD, and a decrease in the conductivity, as the organic acids are consumed.

The resulting anaerobic decomposition is characterized by lower temperatures (38 to 54°C or 100 to 130°F), lower CO_2 concentrations (40 to 48 percent), and significantly higher CH_4 concentrations (45 to 57 percent) than the generally aerobic phase of decomposition. Anaerobic decomposition will continue until all of the volatile organic acids are depleted or until O_2 is reintroduced into the waste, stimulating a resumption of aerobic decomposition of the remaining large polymeric materials and a new degradation cycle. Reverting to aerobic conditions temporarily retards CH_4 gas generation.

Figure A-2 illustrates the evolution of LFG by biological processes.

2.1.4 Chemical Reactions
Chemical reactions between materials in the waste can release gases. Such reactions are likely to occur in hazardous waste landfills unless considerable care is taken not to mix incompatible materials. Older landfills which have received hazardous wastes in the past and municipal landfills which receive household waste are still subject to unforeseen reactions. For example, aliphatic chlorinated solvents are incompatible with aluminum, so solvent-soaked rags which contact aluminum cans may produce hydrogen chloride gas. This will at least render the surrounding gas highly acidic, and may release some vapor through the landfill to the atmosphere.

Many of the potential reaction problems are relatively buffered by the presence of water. Even some materials which are vapors in their pure state (e.g., vinyl chloride) are relatively soluble in water, so the release rate is dampened. However, unpredictable reactions are possible with so many compounds potentially present. As mentioned above, the heat generated from biological processes also tends to accelerate the release rate of compounds produced by chemical reactions.
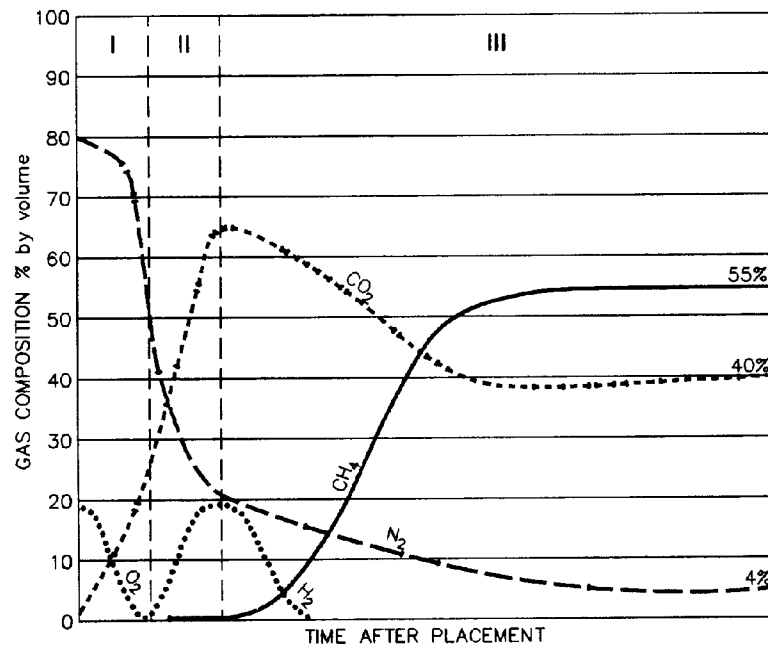
TYPICAL LANDFILL GAS EVOLUTION

FIGURE A-2
(SOURCE 5)

2.2 <u>FACTORS AFFECTING LFG GENERATION</u>
     Gas generation in a landfill is affected by several factors:

- availability of nutrients,
- temperature,
- moisture,
- pH,
- atmospheric conditions,
- age of waste, and
- variation of water table.

     These parameters are discussed below.

2.2.1 <u>Availability of Nutrients</u>
     Bacteria in a landfill require various nutrients for growth;
primary carbon, hydrogen, O_2, nitrogen, and phosphorous
(macronutrients), but also require small amounts of other
elements such as sodium, potassium, sulfur, calcium and magnesium
(micronutrients). The availability of macronutrients in the
landfill mass has an effect on both the volume of water generated
from microbial processes and the composition of the generated
gases. Landfills which accept municipal wastes and use daily
soil cover will, in general, have an adequate nutrient supply for
most microbial processes to proceed. Specialized landfills such
as those in military installations which handle hazardous
materials or munitions wastes only, and which do not use daily
soil cover, may not have sufficient nutrients in the waste to
sustain a microbial population. Once the microbial processes are
established, nutrients are regenerated from sloughing processes
as bacteria die. The primary sources of macronutrients are green
wastes, food wastes and soil cover, but will always be limiting
if not supplemented from an outside source. Some loss of
nutrients can occur as LFG components. The supply of
micronutrients (primarily metals) is less certain, but evidence
from hundreds of landfills suggests that municipal landfills also
contain adequate supplies. The sources of these micronutrients
are usually the trace elements found in almost all soils and many
wastes. The micronutrient requirements are very small and can
usually be met by these trace amounts in the wastes and leached
from the soil cover.

If the nutrient supply is rich, the population of active microbes may become so high that they crowd the available pore spaces and restrict both water flow and LFG flow temporarily. In general, the situation will correct itself because the limited transport will cause some of the bacteria to die of starvation. Nutrient availability can be improved by the addition of sewage sludge, manure or agricultural wastes.

2.2.2 Temperature

Temperature conditions within a landfill influence the type of bacteria that are predominant and the level of gas production. The temperature of the landfill may vary dramatically from one section to another, as the temperature of the material is affected by several factors. The primary factors of temperature variations are depth, compacted density, temperature of the surrounding area, microbial or other chemical activity, water content and climate. Warm landfill temperatures favor CH_4 production; a dramatic drop in activity has been noted at temperatures below 10^0C (50^0F). The optimum temperature range for aerobic decomposition is 54 to 71^0C (130 to 160^0F), while the optimum temperature range for anaerobic bacteria is 30 to 41^0C (85 to $105^\circ F$). Landfill temperatures are reported to be typically in the range of 29.5 to 60^0C (85 to 140^0F) as result of aerobic decomposition, but may be expected to drop to the 19 to 21^0C (65 to 75^0F) range as result of anaerobic activity. The temperature needs to be measured in several locations and an estimate made of the temperature likely to occur in the gas generation zone of interest for design purposes.

2.2.3 Moisture

Moisture content is considered the most important parameter regarding refuse decomposition and gas production. A high moisture content of the waste (between 50 percent and 60 percent) by weight favors maximum CH_4 generation[5]. This is contrary to standard landfill applications, where the waste is maintained as dry as possible in order to minimize leachate production. The moisture content of MSW as received typically ranges from a low of 15 to 20 percent to a high of 30 to 40 percent with an average of 25 percent on a wet weight basis. The moisture content can vary greatly in different zones of the landfill. Very low moisture content, such as the case of solid waste in arid

regions, may prevent decomposition of waste and thus limit gas production. Leachate recirculation (if allowed) would permit control of the moisture inside the landfill. Typically, when a waste achieves a 50 percent moisture (on a wet basis) it has reached the field capacity, and will tend to leach continuously downward thereafter for additional moisture added. In-situ moisture content as high as 70 percent is possible. At this level, a decrease in the efficiency of a gas collection system can be expected.

2.2.4   <u>pH</u>
    The solid material placed in a landfill can vary widely in pH, but usually the average value for municipal waste will be between 5 to 9 standard units. The pH of hazardous wastes can vary widely, and known acids or bases are usually neutralized prior to landfilling. The pH in an active landfill becomes governed primarily by the biological processes described in Section 2.1.

    The pH during CH_4 formation is in the range of 6.5 to 8.0, but the optimum pH of CH_4 fermentation is in the neutral to slightly alkaline range (7.0 to 7.2)[7]. Most landfills have an acidic environment initially, but when the aerobic and acidic anaerobic stages have been completed, the methanogenic processes return the pH to approximately neutral (7 to 8) due to the buffering capacity of the system pH and alkalinity.

    One concern during the acidic stages of the biological process is that the reduced pH will mobilize metals which may leach out of the landfill, or become toxic to the bacteria generating the gas. This is of particular concern where it is known that heavy metals are being placed in the landfill in large quantities. Enhancement of gas production can be achieved by carefully screening the types and amounts of wastes admitted to the landfill; i.e., exclusion of toxic or inhibitory materials, and size reduction of refuse materials. In some cases, the addition of sewage sludge, manure or agricultural wastes during refuse placement would improve CH_4 gas generation.

Military landfills are not generally producing a great quantity of CH_4 gas. Therefore, enhancement of CH_4 gas production is usually not practiced; the gas collection system is designed primarily to prevent the release of gases to comply with the state regulations.

2.2.5 Atmospheric Conditions
The atmosphere affects the conditions in the landfill in three ways: temperature, barometric pressure and precipitation.

In a landfill where soils are used for cover layer, the air temperature not only affects the surface layer of the waste but may have an impact into the deeper layers, because the air permeability will generally be higher in the landfill. Cold climates will reduce biological activity in the surface layers, reducing the volume of gas generated. Deeper in the wastes, the surface temperature effects are often overcome by the heat generated by bacterial activities.

The atmospheric pressure influence is also stronger than would occur in soil systems, where the normal surface air interaction with the soil extends about 6 inches. Until the waste is consolidated to a typical soil density, the barometric pressure can affect the wastes near the surface by drawing air in or venting gas out of the top layer. Wind will also affect the diffusion rate deeper in the landfill by reducing the surface concentration of gas components and creating advection near the surface.

Precipitation dramatically affects the gas generation process by supplying water to the process and by carrying dissolved O_2 into the waste with the water. As the water percolates through the waste, it also extracts materials such as organics or metals as described above. High rates of precipitation may also flood sections of the landfill, which will obstruct gas flow.

In a landfill where geomembrane is used for final cover, the geomenbrane will isolate the waste and minimize many of the atmospheric effects described above.

2.2.6 <u>Age of Waste</u>
The three stages of biological degradation discussed in Chapter 2 have a primary influence on the gas generation rate. During the aerobic phase, the waste is close to the surface and the generated gas is difficult to capture. Aerobic metabolism is oxidative and generally more complete and rapid than anaerobic processes, so the initial rate of CO_2 production is relatively high. As the waste becomes depleted in O_2 and the acidic processes dominate, the LFG production rate decreases. When the acids have been consumed and the methanogens become dominant, the LFG production rate rises again through a peak and then stabilizes. The ideal time to start collecting LFG is at the beginning of site closure. This usually represents the maximum gas generation point, and gas quantities should remain significant for as long as a 10 years. After the landfill closes, the gas generation rate decreases as the organic substrate is consumed and not replaced. It may take as long as 50 years, however, for gas production to cease.

2.2.7 <u>Variation of Water Table</u>
The local geology which will affect the gas-generation rate is the depth and seasonal variation of the water table. Landfills are almost always designed to exist completely above the local water table; if the seasonal high water reaches the bottom of the fill, the hydraulic pressure will affect the waste, and LFG production, in several ways:

- The pressure gradient may lift a liner system and rupture the liner, permitting air and water to penetrate the waste pack;

- Air movement will be stopped in any saturated zone which may be created in the waste;

- Biological activity may stop, change form as oxygenated water is introduced, or be enhanced by the presence of "fresh" water in the leachate; or

- Rupture in the liner may permit leachate to drain from the fill as the water table lowers after reaching its high point.

2.3 <u>TRANSPORT MECHANISMS</u>

The nature of the specific transport mechanism depends on the type of waste (solid or liquid) exposed to the atmosphere. For liquids, the principal release mechanism will be governed by Henry's Law for dilute aqueous solutions. Each compound present has a different constant describing the equilibrium partitioning between the solution and the vapor phase. Many of the volatile organic compounds (VOCs) which may be present (see Table A-1) have high Henry's Law constants; they would preferentially migrate to the vapor phase and out of the landfill. During the landfilling process, this migration is accelerated by the effects of mixing, because the liquid surface (even in a solid matrix) is exposed to the ambient air more frequently.

Several physical mechanisms describe the behavior of volatile compounds as they may be released into the atmosphere from a landfill. The transport may occur by the three principal mechanisms:

- molecular effusion,
- diffusion, and
- convection.

These transport mechanisms are discussed below.

2.3.1 <u>Molecular Effusion</u>

Molecular effusion occurs at the surface boundary of the landfill with the atmosphere. When the material has been compacted, and not has been covered, effusion is the process by which diffused gas releases from the top of the landfill.

For dry solids, the principal release mechanism is direct exposure of the waste vapor phase to the ambient atmosphere. Any volatile liquid constituents which coat the soil surface would be released according to Raoult's Law, which predicts the release rate based on the vapor pressure of the compounds present. Essentially the constant in Raoult's Law describes the

partition coefficient between a pure liquid compound and its
vapor phase.

Raoult's Law. The vapor-pressure depression of a
constituent is directly proportional to the concentration of
particles in solution. In other words, the partial vapor
pressure of a constituent in a gaseous mixture is equal to the
mole fraction of that constituent in the solution times the vapor
pressure of the pure constituent i, which is a function of
temperature. Raoult's Law is presented by the following
formula:

$$P_v = X_i * P_o \qquad\qquad (2-2)$$

where,

P_v = partial pressure of a compound in gaseous mixture, atm

X_i = concentration of compound in solution, mole
fraction

P_o = vapor pressure of the compound in pure state, atm

Vapor Pressure. Liquid molecules that possess sufficient
kinetic energy are projected out of the main body of a liquid at
its free surface and pass into vapor. The pressure exerted by
this vapor is known as the vapor pressure.

The vapor pressure of a given compound is the single most
significant factor affecting the performance of an off-gas
collection system. The vapor pressure of water at 20°(68°F) is
.34 KN/m^2(0.399 psi). In general, compounds which exhibit vapor
pressure greater than 0.5 mm Hg (0.27 in. H_2O) are appropriate
for off-gas collection. Conversion units of the pressure are
given below:

1 newton	=	0.2248 pounds
1 pound	=	231 cm of water column (at 4°C)
1 mm Hg	=	0.5353 inches of water (at 4°C)
10^5 newton/m^2	=	100 KPa

One physical effect on the release rate from the surface is
wind speed. As discussed in Section 2.3.2, wind serves to keep
the ambient concentration at or near zero, which creates a
concentration gradient for material to migrate to the surface.

Wind is also the dispersion mechanism to move the constituents into the surrounding area.

2.3.2 Diffusion

Molecular diffusion occurs in gas systems when a concentration difference exists between two different locations within the gas. Diffusive flow of gas is in the direction in which its concentration decreases. The concentration of a volatile constituent in the LFG will almost always be higher than that of the surrounding atmosphere, so the constituent will tend to migrate to a lower concentration area (the ambient air). Wind often serves to keep the surface concentration at or near zero, which renews the concentration gradient between the surface and the landfill on a continuing basis and thus promotes the migration of vapors to the surface. Geomembrane caps on landfills will have a significant effect on diffusion, because the geomembranes isolate the transport mechanism between the surrounding atmosphere and the landfill.

The rate of diffusion is affected by the vapor density, but the concentration gradient will tend to overcome small differences in density. Specific compounds exhibit different diffusion coefficients, which are the rate constants for this transport.

The published diffusion coefficients have been calculated using open paths between one vapor region (concentration) and another, which is not the case for landfills. The trapped gas must travel a tortuous path to reach the surface because it must travel around all the solids and liquids in its path; thus, the published diffusion coefficients for the constituents must be used with care in detailed design work. They serve more as relative indicators, and are one contributing factor to the monitoring and modeling described in Sections 2.7 and 4.7.

2.3.3 Convection

Convective flow occurs where a pressure gradient exists between the landfill and the atmosphere; gas will flow from higher pressure to lower pressure regions, and also a flow from the landfill to the atmosphere. Where it occurs, convective flow of gas will overwhelm the other two release mechanisms in

its ability to release materials into the atmosphere. The source
of the pressure may be the production of vapors from
biodegradation processes, chemical reactions within the landfill,
compaction effects, or CH_4 generation at the lower regions of the
landfill which drive vapors toward the surface. Variations in
water table elevations can also create small pressure gradients
which either push material out (rising tide) or draw material in
(falling tide). Even changes in barometric pressure at the
surface can have an impact on the convective flow of gas. The
rate of gas movement is generally orders of magnitude faster for
convection than for diffusion. For a particular gas, convective
and diffusive flow may be in opposing directions, resulting in an
overall tendency toward cancellation. However, for most cases of
LFG gas recovery, diffusive and convective flows occur in the
same direction. Figure A-3 illustrates the transport mechanisms.

2.4   FACTORS AFFECTING LFG TRANSPORT MECHANISMS
      LFG transport is affected by the following factors:

- permeability,
- depth of groundwater,
- condition within the waste,
- moisture content,
- man-made features, and landfill liner and cap systems.

2.4.1 Permeability or Intrinsic Permeability
      A coefficient of permeability, k, is often used to describe
the rate of discharge of the fluid (liquid or gas) under
laminar-flow (non-turbulent) conditions and at a standard
temperature (usually 20°C or 68°F) through a unit cross-sectional
area of a porous medium under a unit hydraulic gradient. The LFG
permeability is a function of both its intrinsic (k_i) and
relative (k_r) permeabilities.

      The intrinsic permeability coefficient, k_i, is a measure of
the ease with which a porous medium can transmit LFG, water, or
other fluid through its media. The intrinsic permeability is
specific for each landfill, and is a function only of the porous
medium. The dimensions, in length squared, may be expressed in
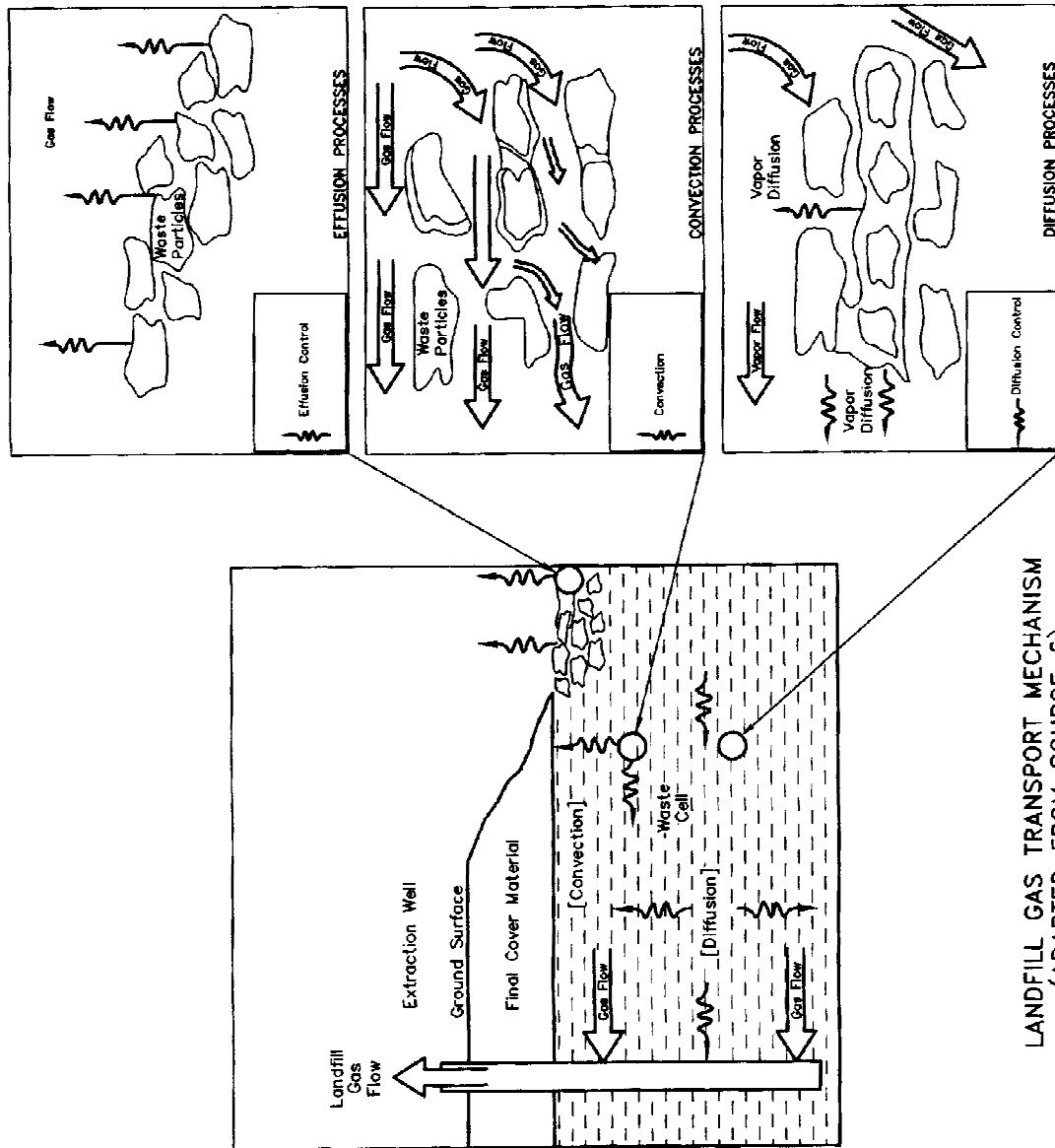
LANDFILL GAS TRANSPORT MECHANISM
(ADAPTED FROM SOURCE 6)
FIG. A-3

units of darcies: 1 darcy = $9.87 \times 10^{-9} cm^2$. The permeability coefficient reported for Palos Verdes Landfill is 20 darcies [5].

The relative permeability is a dimensionless number and is expressed as a fraction of the maximum permeability value that the medium can exhibit for a given fluid. Gas permeability can be measured or estimated by a variety of methods, one of which is presented in Section 4.2.5.5.

The permeability distribution to gas has a profound influence on gas flow rates and gas recovery rates. Coarse-grain refuses typically exhibit large values of gas permeability and more uniform gas flow patterns. Both of these factors tend to promote increased LFG recovery rates. By contrast, fine-grained refuses are characterized by small values of gas permeability and gas flow patterns which are primarily restricted to macropores or secondary permeability zone such as fractures.

2.4.2 Depth of Groundwater

The water table surface tends to act as a no-flow boundary for gas flow within the unsaturated zone. As a result, it is generally used to estimate the thickness of the zone from which a gas can be moved.

The depth to groundwater as well as seasonal variations need to be evaluated during the predesign process to evaluate the well construction requirements as well as the potential for water table upwelling (i.e., the upward rise of the water table toward a vacuum well screened in the unsaturated zone). The potential rise in the water table that can occur at a location is expressed as an equivalent water column height (in cm H_2O). The limit of upwelling, z (cm) can thus be calculated as:

$$h_{rise} = 1033(1-P_r) \qquad (2-3)$$

where,

h_{rise} = increase in the water table surface, cm of water

P_r = pressure reading as a function of the radial distance from the vertical extraction well, atm

1033   =   conversion from 1 cm of water vacuum
pressure to 1 atmosphere.

Upwelling is not a significant concern in more permeable formations, as the applied vacuum will have little influence. In less permeable formations, however, upwelling can be significant and should be quantified for efficient gas system design and operation.

2.4.3 Conditions Within the Waste

The distribution and occurrence of waste and debris within the unsaturated zone greatly affects gas migration and recovery rates. The conditions within the waste (solid matrix) which may affect soil gas transport include:

Heterogeneities. Heterogeneities are caused by spatial variations in solid matrix type, layering, unusual refuse composition and moisture content. Due to the heterogeneous nature of the landfill environment, there will be some acid-phase anaerobic decomposition and some aerobic decomposition occurring simultaneously in any large-scale landfill, along with the methanogenic decomposition. During the operation of an off-gas collection system, these variations may influence LFG quality, gas flow patterns and ultimately gas recovery rates within the landfill.

Porosity. Landfill solid waste's porosity (n) is a ratio of the void volume to the total volume of the porous medium, usually expressed as a decimal fraction or percent. Waste pores can be expressed as a decimal fraction or percent. Waste pores can be occupied by gas, water, and/or bacteria. Porosity can be calculated from the bulk density of the waste, which is the dry weight of waste per bulk volume (i.e.,by following formula:

$$n = 1 - (D_b / D_s) \qquad\qquad (2\text{-}4)$$

where,
    n = waste porosity, dimensionless
    D_b = bulk density of the waste, kg/m^3
    D_s = density of the particle, kg/m^3

The waste porosity of the landfill ranges between 0.04 to 0.10.

The effective porosity is a measure of a waste's ability to transmit air. The effective porosity provides a more useful measure of the rate at which gas is recovered compared to porosity, however. The effective porosity must be quantified in the laboratory and results may be difficult to reproduce. An indirect measure of the effective porosity can be performed during air-phase permeability pilot testing, if conducted.

Moisture Retention. The moisture content of the solid matrix influences the magnitude of the air phase permeability. Water competes with air to occupy pore space within the solid matrix and ultimately reduces the ability of vapors to migrate through the landfill due to a reduction in the air pathway. This reduction may decrease gas recovery rates.

2.4.4 Man-Made Features

In some instances, underground utilities such as storm and sanitary sewers or the backfill material associated with these features may produce short circuiting of air flow associated with an off-gas collection system. As a result, air flow may be concentrated along these features rather than within the zone requiring collection. In addition, these features may also provide migration pathways for both free-phase liquids and vapors within the unsaturated zone. As a result, the orientation and geometry of these features may dictate the direction in which the liquids or vapors migrate.

2.4.5 Landfill Cap and Liner Systems

The components of a hazardous waste landfill cap generally consist of a top layer composed of a vegetated or armored surface component and select fill, a drainage layer, low permeability layer composed of a geomembrane over a low permeability soil component, and a random fill layer overlaying the waste. In addition to the benefit which landfill caps provide for the final closure of landfills, they also provide a significant improvement to the LFG collection by allowing maximum recovery of LFG from all portions of the landfill via

elimination of the need for an exclusion of few feet from cover (buffer zone).

In active collection systems, whether with vertical or horizontal collectors, a geomembrane cap will preclude the intrusion of any air into the refuse. Higher operating vacuum can, therefore, be applied to the gas collection system without danger of overdrawing the gas. Thus the effective radius (reach) of influence of each well is increased.

Landfill liners consist of natural low permeability geologic formations, recompacted clay liners, geomembranes, and geosynthetic clay liners. In addition to prevent the migration of LFG to the surrounding areas, the significance of liners with respect to the LFG collection is to prevent groundwater and/or other gases from the subsurface from being pulled into the LFG collection system.

2.5   CHARACTERISTICS OF LFG
      The characteristics of LFG include:

   ● physical characteristics, and
   ● chemical characteristics.

These characteristics are discussed below:

2.5.1 Physical Characteristics
       Physical characteristics include:

   ● density,
   ● viscosity,
   ● temperature,
   ● heat value content, and
   ● moisture content.

Density. The density of LFG depends on the proportion of gas components present. For example, a mixture of 10 percent hydrogen and 90 percent CO_2, such as might be produced in the first stage of anaerobic decomposition, will be heavier than air, while a mixture of 60 percent CH_4 and 40 percent CO_2, such as might be produced during the methanogenic phase of

decomposition, will be slightly lighter than air. Therefore, the greater the waste density the higher the theoretical yield of LFG per unit volume of void space. Density, **D**, has units in $kg.m^{-3}$ or $lb.ft^{-3}$. Some common values for LFG are given below:

D CH_4 = 0.714 x 10^{-4} kg/m^3 or $1.153 x 10^{-3} lb.ft^{-3}$.

D Composite gas: = 1.07 kg/m^3 or $17.13 lb.ft^{-3}$

Viscosity. Viscosity of a fluid (liquid or gas) is that property which offers resistance to flow due to the existence of internal friction within the fluid. This resistance to flow, expressed as a coefficient of dynamic (or absolute) viscosity is the force required to move a unit area a unit distance.

Absolute viscosity μ is measured in units of $Newton.sec.m^{-2}$; $g.cm^{-1}.sec^{-1}$; Pascal or Newton ($lb.sec.ft^{-2}$; centipoise, or $slug.ft^{-1}.sec^{-1}$). For example, at $0°C$ and 1 atmosphere of pressure, approximate values of μ for CH_4 and composite gas are as follows[5]:

μ CH_4 = 1.04 x 10^{-5} $N.sec.m^{-2}$ or 2.17 x 10^{-7} $lb.sec.ft^{-2}$
μ Composite gas: = 1.15 x 10^{-5} $N.sec.m^{-2}$ or
$\qquad\qquad\qquad$ = 2.40 x $10^{-7} lb.sec.ft^{-2}$

Temperature. Gas temperature varies with location, depth and phase decomposition. This subject is discussed in previous Section 2.2.2.

Heat Value Content. Concentrated mixtures of LFG can be expected to have a calorific value of 500 Btu/cft during the CH_4 generation (methanogenic) stage. This value is about half that of natural gas.

Moisture Content. The amount of moisture in the gas depends on the temperature and pressure and can be saturated or under-saturated. Incoming refuse has an average moisture content of about 25 percent with food and garden components of the waste providing the highest moisture input. Rainfall, surface and groundwater infiltration, and waste decomposition will provide additional moisture.

2.5.2 <u>Chemical Characteristics</u>.
     The composition of LFG depends on the waste type and the stage of decomposition. The amount of LFG produced is generally a function of the type, extent and rate of decomposition. The major environmental conditions which affect the type, rate and extent of biochemical decomposition in a landfill are O_2 availability, moisture, rainfall infiltration, temperature, pH, amount of solid waste, and available microbes. As discussed previously, the major components of the LFG are CH_4, CO_2, NMOC and water vapor. The maximum gas yield has been estimated to be 15,000 cubic yards per ton of waste, with an average estimated gas composition by volume of 54 percent CH_4 and 46 percent CO_2 and trace amounts of NMOCs.

2.5.2.1 <u>Methane</u>
     A major constituent of LFG is CH_4. CH_4 is lighter than air, colorless and odorless. LFG is flammable due to the presence of CH_4 and can be asphyxiant if present in high concentrations without O_2. CH_4 is explosive at about 5 to 15 percent by volume in air. The presence of CO_2 affects these ranges although little significant change occurs in the lower limit of the range.

2.5.2.2 <u>Carbon Dioxide</u>
     Another major constituent of LFG is CO_2. CO_2 is heavier than air, colorless, and odorless. CO_2 can be a simple asphyxiant and health hazard if present in high concentrations.

2.5.2.3 <u>Non-Methane Organic Compounds (NMOC)</u>
     Many minor constituents are present in LFG at low concentrations. Trace gases are produced by the complex interaction of the physical, chemical, and biological processes occurring within the waste. LFG contains a variety of NMOC including:

- benzene,
- toluene,
- ethylbenzene,
- vinyl chloride,
- dichloromethane,
- trichloroethylene,

- 1,2,-cis dichloroethylene, and
- tetrachloroethylene.

These compounds are widely used in industry and are found in common household products or used in their manufacture.

2.5.2.4 Water Vapor
Gas created during the decomposition of organic compounds typically includes between 4 and 7 percent by volume of water vapor. Temperatures are typically elevated over ambient during biological decomposition and increase the evaporation of water into the LFG. Water vapor content of LFG will depend on the system temperature and pressure and could be saturated under landfill conditions.

2.5.2.5 Others
Hydrogen is produced during waste decomposition, particularly during initial anaerobic conversion of mixed organic acids to acetic acid. Significant amounts of hydrogen are later consumed in the formation of CH_4. Hydrogen is flammable between 4 and 74 percent, by volume, in air. The presence of CO_2 affects these ranges although little significant change occurs in the lower limit of the range. A typical nonmethane LFG composition is presented in Table A-2.

2.6 LFG CONDENSATE
2.6.1   Source of LFG Condensate
LFG condensate accumulates in two areas:

- gas collection systems, and
- gas processing systems.

Gas condensate forms in the collection systems as the gas undergoes changes in temperature and pressure. As LFG moves through the collection system, the gas cools and the various constituents condense out of the gas. The condensed material is composed principally of water, organic compounds, and traces of inorganics. Depending on the concentration of hydrocarbons, the organic compounds are generally not soluble in water and separate into aqueous and hydrocarbon phases.

TABLE A-2
Summary of Nonmethane Organic Compounds Found in Landfill Gas

Chemical Name	No. of Times Quantified	Average Conc. Detected ppm	Highest Conc. ppm	Lowest Conc. ppm
Ethane	26	252.63	1780	0
Toluene	40	59.34	758	0.2
Methylene Chloride	37	24.5	174	0
Hydrogen Sulfide	3	252.97	700	11
Ethylbenzene	31	21.73	428	0.15
Xylene	2	333.85	664	3.7
1,2 - Dimethyl Benzene	1	588	588	588
Limonene	1	470	470	470
Total Xylene Isomers	27	17.11	70.9	0
α-Pinene	1	446	446	446
Dichlorodifluoromethane	31	13.1	43.99	0
Ethylester Butanoic Acid	1	398	398	398
Propane	26	13.59	86.5	0
Tetrachloroethene	39	8.43	77	0
Vinyl Chloride	42	7.71	48.1	0
Methylester Butanoic Acid	1	305	305	305
Ethylester Acetic Acid	1	282	282	282
Propylester Butanoic Acid	1	253	253	253
1,2 - Dichloroethene	37	6.33	84.7	0
Methyl Ethyl Ketone	27	8.17	57.5	0
Thiobismethane	1	210	210	210
Methylcyclohexane	2	99.7	197	2.4
Trichloroethene	44	3.98	34	0.01
Nonane	1	167	167	167
Benzene	45	3.6	52.2	0
Ethanol	1	157	157	157
Acetone	26	5.94	32	0
2 - Butanol	1	152	152	152
Octane	1	152	152	152
Pentane	26	5.64	46.53	0
Hexane	26	5.33	25	0
Methylester Acetic Acid	1	136	136	136
1 - Methoxy - 2 Methyl Propane	1	136	136	136
2 - Butanone	1	129	129	129
1,1 - Dichloroethane	33	3.51	19.5	0

TABLE A-2
Summary of Nonmethane Organic Compounds Found in Landfill Gas

Chemical Name	No. of Times Quantified	Average Conc. Detected ppm	Highest Conc. ppm	Lowest Conc. ppm
1 - Butanol	1	100	100	100
Butane	26	3.68	32	0
4 - Methyl - 2 - Pentanone	1	89	89	89
2 - Methyl Propane	1	84	84	84
1 - Methylethylester Butanoic Acid	1	69	69	69
2 - Methyl, Methylester Propanoic Acid	1	69	69	69
Carbon Tetrachloride	37	1.85	68.3	0
Chloroethane	29	2.03	9.2	0
1,1,3 Trimethyl Cyclohexane	1	57	57	57
2 - Methyl - 1 - Propanol	1	51	51	51
1,2 - Dichloroethane	37	1.3	30.1	0
Trichlorofluoromethane	46	0.99	11.9	0
Chloromethane	30	1.38	10.22	0
2,5 Dimethyl Furan	1	41	41	41
2 - Methyl Furan	1	40	40	40
Chlorodifluoromethane	27	1.35	12.58	0
Propene	1	36	36	36
Methyl Isobutyl Ketone	26	1.38	11.5	0
Ethyl Mercaptan	3	11.93	23.8	1
Dichlorofluoromethane	28	1.2	26.11	9
1,1,1 - Trichloroethane	38	0.84	9	0
Tetrahydrofuran	1	30	30	30
Ethylester Propanoic Acid	1	26	26	26
Bromodichloromethane	29	0.71	7.85	0
Ethyl Acetate	1	20	20	20
3-Methylhexane	1	20	20	20
C10H16 Unsaturated Hydrocarbon	1	15	15	15
Methylpropane	1	12	12	12
Chlorobenzene	29	0.38	10	0
Acrylonitrile	26	0.32	7.4	0
Methylethylpropanoate	1	7.3	7.3	7.3
1,1 - Dichloroethene	32	0.23	3.1	0
Methyl Mercaptan	3	1.87	3.3	1
1,2 - Dichloropropane	28	0.12	1.8	0
1 - Propyl Mercaptan	2	1.55	2.1	1

TABLE A-2
Summary of Nonmethane Organic Compounds Found In Landfill Gas

Chemical Name	No. of Times Quantified	Average Conc. Detected ppm	Highest Conc. ppm	Lowest Conc. ppm
Chloroform	36	0.08	1.56	0
1,1,2,2 - Tetrachloroethane	28	0.1	2.35	0
1,1,2,2 - Tetrachloroethene	2	1.33	2.6	0.05
2 - Chloroethylvinyl Ether	28	0.08	2.25	0
t - Butyl Mercaptan	2	0.64	1	0.28
Dimethyl Sulfide	2	0.55	1	0.1
Dichlorotetrafluoroethane	1	1.1	1.1	1.1
Dimethyl Disulfide	2	0.55	1	0.1
Carbonyl Sulfide	1	1	1	1
1,1,2-Trichloro 1,2,2-Trifluoroethane	1	0.5	0.5	0.5
Methyl Ethyl Sulfide	1	0.32	0.32	0
1,1,2 - Trichloroethane	28	0	0.1	0
1,3 - Bromochloropropane	1	0.01	0.01	0.01
1,2 - Dibromoethane	2	0	0	0
C-1,3 - Dichloropropene	2	0	0	0
t-1,3 - Dichloropropene	2	0	0	0
Acrolein	26	0	0	0
1,4-Dichlorobenzene	28	0	0	0
Bromoform	28	0	0	0
1,3 - Dichloropropane	26	0	0	0
1,2 - Dichlorobenzene	29	0	0	0
1,3 - Dichlorobenzene	29	0	0	0
Dibromochloromethane	28	0	0	0
Bromomethane	28	0	0	0
References 3				

Gas recovery systems not only generate condensate in the collection system, but also in gas energy and processing plants. The production of condensate could be through natural or artificial cooling of the gas, or through physical processes such as expansion. Coolers are generally not used. At the surface, typical LFG systems include a condensate collection pot which removes a portion of the entrained water from the vapor prior to entering the vacuum pump or blower. A mist eliminator further removes liquid droplets entrained in the gas.

2.6.2 Condensate Quality
The quality of gas condensate is a function of:

- The nature,
- Age and quality of refuse in the landfill,
- the amount of moisture or liquid in the landfill,
- temperature differences,
- landfill size and configuration,
- type of liner and/or cover materials, and
- climatic conditions.

There is no comprehensive data base on the chemical and physical characteristics of LFG condensate. Data that have been published show that the aqueous phase of LFG condensate generally passes the Toxicity Characteristic Leaching Procedure (TCLP) regulatory limits. If a non-aqueous phase liquid is present in the condensate, this fraction has been found to fail ignitability testing. Landfills that have been operating principally as a municipal landfill are rarely found to have a non-aqueous phase fraction.

An EPA study[3] provided baseline data on condensate characteristics and chemical analyses on each of the aqueous and hydrocarbon phases. Of the 94 organic compounds identified in six LFG condensate samples, 49 were priority pollutant compounds. Eleven of these compounds were found in every sample in either the aqueous or organic phase: benzene, toluene, phenol, ethyl benzene, benzyl alcohol, bis (2-chloroisopropyl) ether, bis (2-ethylhexyl) phthalate, naphthalene, N-nitrosodimethylamine, 2, 4-dimethylphenol, and 4-methylphenol. The EPA study also identified 15 compounds found in the condensate samples which are on the

Toxicity Characteristic (TC) list. These constituents are listed in Table A-3.

Based on the limited condensate data which are available, it is likely that the hydrocarbon or organic phase of the condensate is ignitable, and thus, should be considered hazardous by RCRA standards. Ignitable wastes are those with a flash point below 60^0C (140^0F). Because of the variability in the existing data, each phase of the LFG stream at each site should be tested to determine the potentially hazardous constituents and their effect on the collection and treatment systems.

2.6.3 <u>Mathematical Description of Gas Flow</u>

Darcy*s Law has often been used to describe laminar flow of fluids through porous media, but it has also been applied to the flow of landfill gases toward a production well. Darcy*s Law for radial flow of landfill toward a recovery well may be expressed mathematically, as follows(5):

$$V_r = - k*\frac{dh}{dl} \qquad\qquad (2-5)$$

where,

      1   = radial distance from the recovery well, m
      V_r = apparent gas velocity at distance 1, in/sec
      k   = permeability coefficient, m/sec
      h   = hydraulic head, m

$$with\ h = \frac{p}{(} + z \qquad\qquad (2-6)$$

where,

      p = total pressure at distance 1, N/m^2
      (= specific weight of the gas, kg/m^3 or N/m^3
      z = elevation above some arbitrary datum, m

The derivative, dh/dl, represents the hydraulic gradient at distance 1. The negative sign indicates that flow is of decreasing hydraulic head toward the recovery well [8].

The pressure/pressure head, p, can have different units as follows:

TABLE A-3
Toxicity Characteristic Ust Compounds Found In LFG Condensate

Compound	Presence		Regulatory Level[1] (mg/l)	Regulatory Level Exceeded	
	Aqueous	Organic		Aqueous	Organic
Volatile Organic Compounds					
Benzene	X	X	0.5	X	X
2-Butanone (MEK)	X		200.0	X	
Carbon tetrachloride	X		0.5	X	
Chlorobenzene	X[2]	X	100.0		X
Chloroform	X[2]	X	6.0		X
1,2-Dichloroethane			0.5		
1,1-Dichloroethene			0.7		
Tetrachloroethylene	X	X	0.7	X	X
Trichloroethylene	X	X	0.5		X
Vinyl chloride			0.2		
Acid and Base/Neutral Compounds					
Cresols, Total			200		
1,4-Dichlorobenzene	X	X	7.5		X
2,4-Dinitrotoluene			0.13[3]		
Hexachlorobenzene			0.13[3]		
Hexachlorobutadiene			0.5		
Hexachloroethane			3.0		
Nitrobenzene	X		2.0		
Pentachlorophenol	.		100.0		
Pyridine			5.0[3]		
2,4,5-Trichlorophenol			400.0		
2,4,6-Trichlorophenol			2.0		

[1] Regulatory Level according to the TC List in 40 CFR 261.24 (Table 1)
[2] Detected at levels too low to quantify
[3] Quantitation limit is greater than the calculated regulatory level. The quantitation limit therefore becomes the regulatory limit.

```
1 bar       =     10^5 N.m^{-2}
            =     0.987 atmospheres
            =     14.5 psi
            =     10^6 dynes.cm^{-2}
            =     100 KPa
            =     1020 cm column of water
            =     75.01 cm column of mercury (Hg)
```

Darcy*s Law applies only to laminar flow; that is, the resistive forces of viscosity predominate. Reynold*s number is usually used to verify the laminar flow. Reynold*s number is defined by the following equation:

$$Re = \frac{p \cdot v \cdot D}{\mu} \qquad\qquad (2\text{-}7)$$

where,

Re = Reynold*s number, dimensionless

μ = absolute viscosity of the fluid, Pa.sec.m^{-2}

D = density of the fluid, kg.m^{-3}

v = velocity of flow, m.sec^{-1}*

D = mean grain diameter of the porous medium, m

Previous works found that laminar flow occurs when the Reynold*s number is in the range of 1 to 10. This means that Darcy* law applies only to very slowly moving water/gas. Maximum velocity, v, at the refuse/recovery well interface was found to be in order of 0.3 cm/sec[7].

Other references assume laminar flow conditions if the change in pressure ()P) is less than 12 inches of water column.

2.7 <u>ESTIMATION OF GAS EMISSION</u>

LFG emissions are site-specific and are a function of both controllable and uncontrollable factors. It is, therefore, difficult to accurately predict the rate of LFG emission from a landfill. The current approach to modeling the gas generation is to employ a simplified model, consistent with fundamental principles. Several models are available for estimating the LFG generation rate using site-specific input parameters. Three relatively simplistic models are the Palos Verdes, Sheldon

Arleta and Scholl Canyon models. The Palos Verdes and Sheldon
Arleta will not be discussed in this ETL. Details on these models
can be found elsewhere[5]. There are other models such as the
Theoretical model and the GTLEACH-I model. The GTLEACH-I treats
the landfill as a fixed-film microbial treatment process
operating in batch-wise configuration with a continuous dilution
and wash out. However, the GTLEACH-I model requires extensive
input data which include numerous initial concentrations,
moisture content, and leachate flow rate [4]. Due to complicated
input data requirements, the GTLEACH-I model will not be
discussed in this ETL.

2.7.1 <u>Scholl Canyon Model</u>
     The Scholl Canyon Model is a model which assumes that CH_4
generation is a function of first-order kinetics. This model
ignores the first two stages of bacterial activity and is simply
based on the observed characteristics of substrate-limited
bacterial growth. The parameters of this model are empirically
determined by fitting the empirical data to the model to account
for variations in the refuse moisture content and other landfill
conditions. The gas production rate is assumed to be at its peak
upon initial placement after a negligible lag time during which
anaerobic conditions are established and decreases exponentially
(first-order decay) as the organic content of the waste is
consumed. Average annual placement rates are used, and the time
measurements are in years. The model equation takes the form:

$$Q_{CH4} = L_0 * R (e^{-kc} - e^{-kt}) \qquad (2-8)$$

Where:
Q_{CH4} = CH4 generation rate at time t, m^3/yr
L_0 = potential CH_4 generation capacity of the
          waste, m^3/Mg
R = average annual acceptance rate of waste,
          Mg/yr
k = CH_4 generation rate constant, 1/yr
c = time since landfill closure, yr (c=0 for
          active landfill)
t = time since initial waste placement, yr.

The model could be further refined by dividing the landfill into smaller submasses to account for the landfill age over time. If a constant annual acceptance rate (R) is assumed, the CH_4 generated from the entire landfill (sum of each submass contribution) is maximum at the time of landfill closure. Lag time due to the establishment of anaerobic conditions could also be incorporated into the model by replacing "c" with "c + lag time" and "t" by "t + lag time". The lag time before which anaerobic conditions are established may range from 200 days to several years[11].

The refined Scholl Canyon Model equation then takes the following form:

$$Q = 2 * k * L_0 * R \, (e^{-k(t - lag)}) \qquad\qquad (2-9)$$

Where:
Q	=	LFG generation rate at time t, m^3/yr
L_0	=	potential CH_4 generation capacity of the waste, m^3/Mg
R	=	average annual acceptance rate of waste, Mg/yr
k	=	CH_4 generation rate constant, 1/yr
t	=	time since initial waste placement, yrs.
lag	=	time to reach anaerobic conditions, yrs.

2.7.2 Theoretical Models

The theoretical CH_4 generation capacity (L_0) can be determined by a stoichiometric method[11] which is based on a gross empirical formula representing the chemical composition of the waste. If a waste contains carbon, hydrogen, O_2, nitrogen and sulfur (represented by $C_aH_bO_cN_dS_e$), its decomposition to gas is shown as:

$$C_aH_bO_cN_dS_e \; \text{---}> \; vCH_4 + wCO_2 + xN_2 + yNH_3 + zH_2S + humus \qquad (2-10)$$
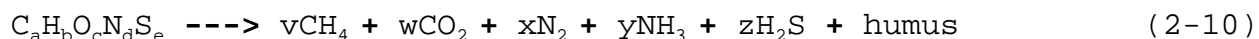
The composition of LFG, during anaerobic conditions, is approximately 50 percent CH_4, 40 to 50 percent CO_2 and 1 to 10 percent other gases.

The value of L_0 is most directly proportional to the waste*s cellulose content. The theoretical CH_4 generation rate increases as the cellulose content of the refuse increases. If the landfill conditions are not favorable to methanogenic activity, there would be a reduction in the theoretical value of L_0. This implies that the theoretical (potential) value of CH_4 generation may never be obtained. The obtainable value of for the refuse (or specific waste components) is approximated by performing overall biodegradability tests on the waste under conditions of temperature, moisture, nutrient content, and pH likely to exist in the landfill. Theoretical and obtainable L_0 values have been reported in literature[11] to range from approximately 6 to 270 m^3 CH_4 per metric ton of waste for municipal landfills.

The CH_4 generation rate constant, k, estimates how rapidly the CH_4 production rate falls after the waste has been placed (since the method assumes the rate is at its maximum upon placement). The value of k is strongly influenced by:

- temperature,
- moisture content,
- availability of nutrients, and
- pH.

CH_4 generation increases as the moisture content increases up to a level of 60 to 80%, at which the generation rate does not increase[7]. Values of k obtained from literature, laboratory simulator results, and back-calculated from measured gas generation rates range from 0.003/yr to 0.21/yr[11].

Once these constants have been estimated, the rate of waste placement and the time in the landfill life cycle determine the estimated gas emission rate.

2.7.3 Regression Model
The actual data from 21 U.S. landfills were used to develop a statistical model to estimate the CH_4 gas generation rate[13]. Based on the preliminary data analysis, a linear model appeared to be sufficient to model CH_4 generation rate. Selection of the variables for the regression model was based on the results of

the correlation and scatter plots. For most of the models that use single landfill parameter, the intercept was insignificant. Hence, the simple model was found to be a no-intercept regression model correlating CH_4 recovery rate to the refuse mass according to:

$$Q_{CH4} = 4.52 \ W \tag{2-11}$$

where,

Q_{CH4} = CH_4 flow rate (m3/min)
W = mass of refuse (metric tons)

The regression coefficient (R^2) for this correlation was 0.50. No other variable except the mass of refuse and the depth of the landfill was found to have any effect on the CH_4 production rate. No functional model was found linking CH_4 production to climate variables. The upper and lower 95% confidence limits for the slope in the above equation are 6.52 and 2.52 m3 CH_4 per ton of refuse.

2.7.4 Comparison of the Scholl Canyon and Regression Models
     The characteristics of Scholl Canyon Model are:

●   It is a theoretical model based on a first-order decay equation;

●   It has two adjustable variables; namely L_0, and k which should be developed for each landfill;

●   When the variables are known, the model could be dependable;

●   The model is impractical for use on a global scale where site-specific data are not available.

     The regression model has the following characteristics:

●   It is a simple empirical model based on actual performance data from 21 landfills.

●   It requires only one variable (i.e., quantity of refuse
     in the landfill) to estimate the OH_4 emission rate.

●   Additional observations could be easily added to the
     model to further refine the model.

●   The model may over-estimate the emission rate for
     wastes with low cellulose content, and

●   The model is found satisfactory in estimating CH_4
     production rate on a global basis.

The two models were compared with each other in predicting
the emission rate from the 21 U.S. landfills. The comparison was
made by calculating the ratio of model-predicted to actual
emission rates, the mean and standard deviations of the ratios
from both the regression model and the Scholl Canyon Model are
then obtained. The closer this ratio is to unity, the more
successful the model is in estimating the emission rate. Table A-
4 shows the comparison of the two models. The Scholl Canyon Model
was run with three different values for the potential CH_4
generation capacity (L_0). The Scholl Canyon Model seems to
underpredict the emission in Run 1 where L_0 was 50 m^3/ton. In Run
2, where L_0 is set to 162 m^3/ton, the model is very accurate and
the mean ratio is 1.07. In Run 3, L_0 is assumed at 298 m^3/ton, and
the model overestimates the CH_4 emission rates. The regression
model predicts the emission rate which falls between the Scholl
Canyon Model in Runs 1 and 3. It is important to note that the
regression study uses CH_4 recovery rate as a surrogate for OH_4
emissions. The validity of this substitution is unknown,
therefore the emissions could be both overestimated and
underestimated.

Despite these concerns, the regression model is very simple
and easily adapted to global emissions estimation.

Table A-4

Comparison of Performance of Scholl Canyon and Regression Model

| Site Number | Scholl Canyon Model | | | Regression Model |
	Run 1 Pred/Actual	Run 2 Pred/Actual	Run 3 Pred/Actual	Pred/Actual
1	0.16	0.40	0.73	0.52
2	0.48	1.21	2.23	1.55
3	0.28	0.71	1.31	0.83
4	0.22	0.55	1.01	0.62
5	0.58	1.44	2.66	1.95
6	0.24	0.60	1.10	0.73
7	0.46	1.16	2.14	1.50
8	0.37	0.93	1.71	1.15
9	0.36	0.90	1.67	1.15
10	0.25	0.64	1.17	0.83
11	0.23	0.57	1.05	0.85
12	0.54	1.34	2.47	1.72
13	0.16	0.39	0.72	0.57
16	0.33	0.82	1.52	1.02
17	0.49	1.23	2.26	1.73
20	0.41	1.02	1.88	1.24
21	0.15	0.36	0.67	0.47
22	0.19	0.47	0.87	0.57
23	1.74	4.35	8.00	6.32
24	0.54	1.34	2.46	1.6
25	0.82	2.06	3.79	2.34
Mean	0.43	1.07	1.97	1.39
Std. Deviation	0.34	0.85	1.56	1.24